

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>B32B 27/36, B42D 15/02</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/37849</b> <b>(43) International Publication Date:</b> 16 October 1997 (16.10.97)
<b>(21) International Application Number:</b> PCT/GB97/00708 <b>(22) International Filing Date:</b> 14 March 1997 (14.03.97)  <b>(30) Priority Data:</b> 9607401.8                      10 April 1996 (10.04.96)                      GB  <b>(71) Applicant (for all designated States except US):</b> IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chem- ical House, Millbank, London SW1P 3JF (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> BRENNAN, William, James [GB/GB]; 124 Oxford Road, Linthorpe, Mid- dlesbrough, Cleveland TS5 5EL (GB). RHOADES, Gary, Victor [GB/GB]; Chestnuts, 586 Yarm Road, Eaglescliffe, Stockton-on-Tees, Cleveland TS16 0DS (GB). LAWRENCE, Paul, David [GB/GB]; 139 Trimdom Avenue, Acklam, Middlesbrough, Cleveland TS5 8RJ (GB).  <b>(74) Agents:</b> HUMPHRIES, Martyn et al.; ICI Group Intellectual Property, P.O. Box 90, Wilton, Middlesbrough, Cleveland TS90 8JE (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> MULTILAYER CARD  <b>(57) Abstract</b>  A multilayer card has (i) an opaque polyester film substrate (1) containing 0.2 to 30 % by weight, relative to the total weight of the substrate, of at least one copolyesterether, (ii) an ink-receptive layer (2) on at least one surface of the substrate, and (iii) a cover layer (4) on the surface of the ink-receptive layer and/or surface of the substrate. The presence of the copolyesterether in the substrate reduces the tendency of the card to delaminate in use. Suitable for use, inter alia, in identification, magnetic, credit, pre-paid and smart cards.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SF	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

### Multilayer Card

This invention relates to a multilayer card such as an identification, credit or magnetic card, and in particular to a multilayer card comprising an opaque polyester film substrate.

5 Polyester films, such as polyethylene terephthalate, are of utility in a wide range of applications including magnetic recording media - such as tapes and discs, as supporting substrates for light-sensitive emulsions, pressure-sensitive adhesives and metal layers, as decorative drapes, electrical insulants, packaging films and cards.

10 Polyester films have been used in the production of an identification or magnetic card, such as a credit card, and in particular a "pre-paid card", eg a telephone card, and a "smart card", which is, for example, capable of storing information relating to a number of financial transactions. Such cards are usually constructed of multiple sheets of the same, eg all polyester, or different materials, eg alternative sheets of polyester, such as polyethylene terephthalate and PETG, polycarbonate, polyolefin, polyvinyl  
15 chloride, ABS resin or paper. A card preferably contains at least one opaque layer. We have discovered that the presence of an opaque polyester film in a multilayer card results in a tendency of the card to delaminate in use, with subsequent peeling of the layers.

20 Copolyesterethers have been used in polyester films to improve the flex-crack resistance thereof. EP-A-0437942 describes a transparent polyester film containing a copolyesterether which is suitable for use in packaging applications.

We have now devised a multilayer card comprising an opaque polyester film substrate which exhibits improved resistance to delamination.

25 Accordingly, the present invention provides a multilayer card comprising (i) an opaque polyester film substrate comprising in the range from 0.2 to 30% by weight, relative to the total weight of the substrate, of at least one copolyesterether, (ii) an ink-receptive layer on at least one surface of the substrate, and (iii) a cover layer on the surface of the ink-receptive layer and/or surface of the substrate.

30 The invention also provides a method of producing a multilayer card which comprises forming an opaque substrate by extruding a layer of molten linear polyester comprising an opacifying agent and in the range from 0.2 to 30% by weight, relative to the total weight of the substrate, of at least one copolyesterether, quenching the extrudate, orienting the quenched extrudate in at least one direction, forming an ink  
35 receptive layer on at least one surface of the substrate, applying pictorial and/or written information on the surface of the ink-receptive layer, and forming a cover layer on the surface of the information carrying ink receptive layer and/or surface of the substrate.

The polyester film substrate is a self-supporting film by which is meant a self-supporting structure capable of independent existence in the absence of a supporting base.

A polyester suitable for use in the formation of a substrate layer is preferably a synthetic linear polyester and may be obtained by condensing one or more dicarboxylic acids or their lower alkyl (up to 6 carbon atoms) diesters, eg terephthalic acid, isophthalic acid, phthalic acid, 2,5-, 2,6- or 2,7-naphthalenedicarboxylic acid, succinic acid, sebacic acid, adipic acid, azelaic acid, 4,4'-diphenyldicarboxylic acid, hexahydro-terephthalic acid or 1,2-bis-p-carboxyphenoxyethane (optionally with a monocarboxylic acid, such as pivalic acid) with one or more glycols, particularly an aliphatic or cycloaliphatic glycol, eg ethylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol and 1,4-cyclohexane dimethanol. A polyethylene terephthalate or polyethylene naphthalate film is preferred. A polyethylene terephthalate film is particularly preferred, especially such a film which has been biaxially oriented by sequential stretching in two mutually perpendicular directions, typically at a temperature in the range from 70 to 125°C, and preferably heat set, typically at a temperature in the range from 150 to 250°C, for example as described in GB-A-838708.

The polyester substrate may be unoriented, or preferably oriented, for example uniaxially oriented, or more preferably biaxially oriented by drawing in two mutually perpendicular directions in the plane of the film to achieve a satisfactory combination of mechanical and physical properties. Simultaneous biaxial orientation may be effected by extruding a thermoplastics polymeric tube which is subsequently quenched, reheated and then expanded by internal gas pressure to induce transverse orientation, and withdrawn at a rate which will induce longitudinal orientation. Sequential stretching may be effected in a stenter process by extruding the thermoplastics material as a flat extrudate which is subsequently stretched first in one direction and then in the other mutually perpendicular direction. Generally, it is preferred to stretch firstly in the longitudinal direction, ie the forward direction through the film stretching machine, and then in the transverse direction. A stretched substrate film may be, and preferably is, dimensionally stabilised by heat-setting under dimensional restraint at a temperature above the glass transition temperature thereof.

A copolyesterether employed in the present invention is preferably a block copolymer comprising predominantly a polyester block as a hard segment, and a polyether block as a soft segment.

The hard polyester block is suitably formed by condensing one or more dicarboxylic acids, or ester derivatives or ester forming derivatives thereof, with one or more glycols. The dicarboxylic acid or derivative thereof may be aliphatic, cycloaliphatic or aromatic. Suitable aliphatic or cycloaliphatic dicarboxylic acids include 1,3- or 1,4-cyclohexane dicarboxylic, adipic, glutaric, succinic, carbonic, oxalic and azelaic acids. Aromatic dicarboxylic acids are preferred and include terephthalic, isophthalic, phthalic, bibenzoic and naphthalenedicarboxylic acids, and the dimethyl derivatives thereof. The glycol component may also be aliphatic, cycloaliphatic or aromatic. The glycol is preferably aliphatic or cycloaliphatic. Suitable glycols include ethylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol, 1,6-hexanediol and 1,4-cyclohexane dimethanol.

The polyester block preferably comprises at least one alkylene terephthalate, for example ethylene terephthalate, butylene terephthalate and/or hexylene terephthalate. Butylene terephthalate is particularly preferred. The molecular weight of the polyester block is preferably less than 15,000, more preferably in the range from 440 to 10,000, particularly 660 to 3000, and especially 880 to 1500.

The soft polyether block is a polymeric glycol suitably formed from one or more glycols such as ethylene glycol, 1,2- or 1,3-propanediol, 1,4-butanediol, neopentyl glycol, 1,6-hexanediol and 1,4-cyclohexane dimethanol. The polyether block is preferably a poly(alkylene oxide) glycol, for example poly(ethylene oxide) glycol, poly(1,2- and 1,3-propylene oxide) glycol, poly(tetramethylene oxide) glycol, and random or block copolymers of ethylene oxide and propylene oxide. Poly(tetramethylene oxide) glycol is a preferred component of the polyether block. The molecular weight of the polyether, preferably poly(tetramethylene oxide) glycol, block is preferably in the range from 350 to 10,000, more preferably 600 to 5000, particularly 900 to 2000, and especially 1200 to 1800. In a particularly preferred embodiment of the invention, the copolyesterether comprises, as the soft polyether block, a mixture of poly(tetramethylene oxide) glycol and poly(propylene oxide) glycol, suitably in a ratio of from 1 to 20:1, preferably 5 to 15:1, and more preferably 8 to 12:1. The molecular weight of the poly(propylene oxide) glycol is preferably in the range from 1000 to 5000, more preferably 2000 to 3000.

The ratio of hard:soft block in the copolyesterether is preferably in the range from 10 to 95:5 to 90, more preferably 25 to 55:45 to 75, and particularly 35 to 45:55 to 65 weight %.

In a preferred embodiment of the invention the copolyesterether is dried prior to polyester film substrate formation and/or prior to incorporation in the substrate layer

composition. The copolyesterether may be dried in isolation, or after mixing with one or more of the other components of the substrate layer, eg dried after mixing with the opacifying agent, preferably inorganic filler, more preferably titanium dioxide. The copolyesterether may be dried by conventional means, for example in a fluidised bed, or in an oven, at elevated temperature, under vacuum or by passing through an inert gas, eg nitrogen. The water content of the copolyesterether prior to extrusion of the film forming substrate layer composition and subsequent film formation is suitably in the range from 0 to 800 ppm, preferably 25 to 600 ppm, more preferably 50 to 400 ppm, particularly 100 to 300 ppm, and especially 150 to 250 ppm.

The amount of copolyesterether present in the polyester substrate is preferably in the range from 1 to 20, more preferably 3 to 15, particularly 5 to 12, and especially 6 to 10% by weight, relative to the total weight of the substrate layer. The amount of polyether present in the polyester substrate is preferably in the range from 0.5 to 15, more preferably 1 to 5, and particularly 2 to 4% by weight, relative to the total weight of the substrate layer.

The copolyesterether employed in the present invention preferably has a flexural modulus (measured at 23°C according to ASTM D790) of 200 MPa or less, and more preferably in the range from 50 to 100 MPa. In addition, preferred copolyesterethers have a Shore hardness (measured at 23°C on the D scale according to DIN 53505) of 60 or less, particularly in the range from 35 to 45.

The copolyesterethers can be prepared by conventional polymerisation techniques, which are well known to those skilled in the art.

The polyester substrate is opaque, by which is meant substantially impermeable to light, and preferably exhibits a Transmission Optical Density (TOD) (Macbeth Densitometer; type TD 902; transmission mode) in the range from 0.6 to 1.75, more preferably 0.8 to 1.6, particularly 1.0 to 1.5, and especially 1.1 to 1.4. The aforementioned TOD ranges are particularly applicable to a 300 µm thick substrate.

The polyester substrate is preferably white and suitably exhibits a whiteness index, measured as herein described, of greater than 85, more preferably in a range from 90 to 105, particularly 92 to 100, and especially 94 to 98 units.

The polyester substrate preferably exhibits a yellowness index, measured as herein described, of less than or equal to 3, more preferably in the range from -10 to 0, particularly -8 to -3, and especially -7 to -5.

The polyester substrate is conveniently rendered opaque by incorporation into the synthetic polyester of an effective amount of an opacifying agent. Suitable opacifying

agents include an incompatible resin filler, a particulate inorganic filler or a mixture of two or more such fillers.

By an "incompatible resin" is meant a resin which either does not melt, or which is substantially immiscible with the polyester, at the highest temperature encountered during extrusion and fabrication of the layer. The presence of an incompatible resin usually results in a voided film, by which is meant that the film comprises a cellular structure containing at least a proportion of discrete, closed cells. Suitable incompatible resins include polyamides and olefin polymers, particularly a homo- or co-polymer of a mono-alpha-olefin containing up to 6 carbon atoms in its molecule, for incorporation into a polyester film. For incorporation into a polyethylene terephthalate film, suitable materials include a low or high density olefin homopolymer, particularly polyethylene, polypropylene or poly-4-methylpentene-1, an olefin copolymer, particularly an ethylene-propylene copolymer, or a mixture of two or more thereof. Random, block or graft copolymers may be employed.

The amount of incompatible resin filler present in the polyester substrate is preferably within the range from 2 to 30, more preferably 3 to 20, especially 4 to 15, and particularly 5 to 10% by weight, relative to the total weight of the substrate layer.

Particulate inorganic fillers suitable for generating an opaque polyester substrate include conventional inorganic pigments and fillers, and particularly metal or metalloid oxides, such as alumina, silica and titania, and alkaline metal salts, such as the carbonates and sulphates of calcium and barium. The particulate inorganic fillers may be of the voiding or non-voiding type. Suitable particulate inorganic fillers may be homogeneous and consist essentially of a single filler material or compound, such as titanium dioxide or barium sulphate alone. Alternatively, at least a proportion of the filler may be heterogeneous, the primary filler material being associated with an additional modifying component. For example, the primary filler particle may be treated with a surface modifier, such as a pigment, soap, surfactant coupling agent or other modifier to promote or alter the degree to which the filler is compatible with the substrate polyester.

In a preferred embodiment of the invention the polyester substrate has a degree of voiding in the range from 0 to 15, more preferably 0.01 to 10, particularly 0.05 to 5, and especially 0.1 to 1% by volume. Thus, the polyester substrate is preferably substantially free of voids. The degree of voiding can be determined, for example, by sectioning the film using scanning electron microscopy, and measuring the voids by image analysis. The density of the polyester substrate is preferably in the range from 1.2 to 1.5, more preferably 1.3 to 1.45, and particularly 1.35 to 1.4.

In a particularly preferred embodiment of the invention, the particulate inorganic filler comprises titanium dioxide. Substantially non-voiding titanium dioxide is preferred.

5 The individual or primary inorganic filler, preferably titanium dioxide, particles suitably have a mean crystal size, as determined by electron microscopy, in the range from 0.05 to 0.4  $\mu\text{m}$ , preferably from 0.1 to 0.2  $\mu\text{m}$ , and more preferably of approximately 0.15  $\mu\text{m}$ . In a preferred embodiment of the invention, the primary inorganic filler, preferably titanium dioxide, particles aggregate to form clusters or agglomerates comprising a plurality of inorganic filler particles. The aggregation  
10 process of the primary inorganic filler particles may take place during the actual synthesis of the filler and/or during the polyester and film making process.

The aggregated inorganic filler particles preferably have a volume distributed median particle diameter (equivalent spherical diameter corresponding to 50% of the volume of all the particles, read on the cumulative distribution curve relating volume %  
15 to the diameter of the particles - often referred to as the "D(v,0.5)" value), as determined by laser diffraction, in the range from 0.3 to 1.5  $\mu\text{m}$ , more preferably 0.4 to 1.2  $\mu\text{m}$ , and particularly 0.5 to 0.9  $\mu\text{m}$ .

The size distribution of the inorganic filler particles is also an important parameter, for example the presence of excessively large particles can result in the film exhibiting unsightly 'speckle', ie where the presence of filler aggregates in the film can be  
20 discerned with the naked eye. It is preferred that none of the inorganic filler incorporated into the substrate should have an actual particle size exceeding 30  $\mu\text{m}$ . Particles exceeding such a size may be removed by sieving processes which are known in the art. However, sieving operations are not always totally successful in  
25 eliminating all particles greater than a chosen size. In practice, therefore, the size of 99.9% by number of the inorganic filler particles should not exceed 30  $\mu\text{m}$ , preferably should not exceed 20  $\mu\text{m}$ , and more preferably should not exceed 10  $\mu\text{m}$ . Preferably at least 90%, more preferably at least 95% of the inorganic filler particles are within the range of the volume distributed median particle diameter  $\pm$  0.5  $\mu\text{m}$ , and particularly  $\pm$   
30 0.3  $\mu\text{m}$ .

The amount of inorganic filler incorporated into the polyester substrate desirably should be in the range from 5 to 25, more preferably 10 to 25, particularly 12 to 20, and especially 14 to 16% by weight, relative to the total weight of the substrate layer.

The preferred titanium dioxide particles may be of anatase or rutile crystal form.  
35 The titanium dioxide particles preferably comprise a major portion of anatase, more preferably at least 60%, particularly at least 80%, and especially approximately 100%



by weight of anatase. The particles can be prepared by standard procedures, such as using the chloride process or preferably by the sulphate process.

In one embodiment of the invention the titanium dioxide particles are coated preferably with inorganic oxides such as aluminium, silicon, zinc, magnesium or mixtures thereof. Preferably the coating additionally comprises an organic compound, such as fatty acids and preferably alkanols, suitably having from 8 to 30, preferably from 12 to 24 carbon atoms. Polydiorganosiloxanes or polyorganohydrogensiloxanes, such as polydimethylsiloxane or polymethylhydrogensiloxane are suitable organic compounds.

The coating is applied to the titanium dioxide particles in aqueous suspension. The inorganic oxides are precipitated in aqueous suspension from water-soluble compounds such as sodium aluminate, aluminium sulphate, aluminium hydroxide, aluminium nitrate, silicic acid or sodium silicate.

Particle size of the filler particles described herein may be measured by electron microscope, coulter counter, sedimentation analysis and static or dynamic light scattering. Techniques based on laser light diffraction are preferred. The median particle size may be determined by plotting a cumulative distribution curve representing the percentage of particle volume below chosen particle sizes and measuring the 50th percentile. The volume distributed median particle diameter of the filler particles is suitably measured using a Malvern Instruments Mastersizer MS 15 Particle Sizer after dispersing the filler in ethylene glycol in a high shear (eg Chemcoll) mixer.

In one embodiment of the invention, the polyester substrate comprises an optical brightener. The optical brightener is preferably added in amounts in the range from 50 to 1500 ppm, more preferably 200 to 1000 ppm, and especially 400 to 600 ppm by weight, relative to the weight of the substrate polyester. Suitable optical brighteners include those available commercially under the trade names "Uvitex" MES, "Uvitex" OB, "Leucopur" EGM and "Eastobrite" OB-1.

In a preferred embodiment of the invention, the polyester substrate comprises a blue dye, preferably in amounts in the range from 100 to 3000 ppm, more preferably 200 to 2000 ppm, and especially 300 to 1000 ppm by weight, relative to the weight of the substrate polyester.

The optical brightener and/or blue dye may be included at any stage of the polyester or polyester film production. Preferably the optical brightener and/or blue dye is added to the glycol, or alternatively by subsequent addition to the polyester prior to the formation of the polyester film, eg by injection during extrusion.

The thickness of the polyester substrate is preferably in the range from 25 to 400  $\mu\text{m}$ , more preferably 100 to 350  $\mu\text{m}$ , particularly 250 to 320  $\mu\text{m}$ , and especially 280 to 310  $\mu\text{m}$ .

The components of the substrate layer composition may be mixed together in conventional manner. For example, by mixing with the monomeric reactants from which the polyester is derived, or the components may be mixed with the polyester by tumble or dry blending or by compounding in an extruder, followed by cooling and, usually, comminution into granules or chips. The copolyesterether may be fed separately to the extruder from which the linear polyester is extruded to form the substrate layer.

The ink-receptive layer is preferably a polymeric coating layer which functions to improve the adhesion of inks, dyes and/or lacquers etc to the polyester substrate. The ink-receptive layer preferably comprises at least one ink-receptive polymer. The ink-receptive layer may carry pictorial information, such as an ordinary photograph, and/or written information such as typed script, a signature etc, as appropriate. The ink-receptive layer may be printed on by means of traditional printing processes such as off-set, gravure, silk screen, and flexographic printing, or by writing by hand, or by thermal transfer printing (TTP), or by laser transfer printing (LTP). The chemical composition of the ink-receptive layer may vary over a wide range, and suitable materials include polyesters, polyurethanes, acrylics and styrene-containing polymers.

In one embodiment of the invention the ink-receptive layer suitably comprises a polyester resin, particularly a copolyester resin derived from one or more dibasic aromatic carboxylic acids, such as terephthalic acid, isophthalic acid and hexahydroterephthalic acid, and one or more glycols, such as ethylene glycol, diethylene glycol, triethylene glycol and neopentyl glycol. Typical copolyesters which provide satisfactory properties are those of ethylene terephthalate and ethylene isophthalate, especially in the molar ratios of from 50 to 90 mole % ethylene terephthalate and correspondingly from 50 to 10 mole % ethylene isophthalate. Preferred copolyesters comprise from 65 to 85 mole % ethylene terephthalate and from 35 to 15 mole % ethylene isophthalate, and especially a copolyester of about 82 mole % ethylene terephthalate and about 18 mole % ethylene isophthalate.

The polyester ink-receptive layer may be applied from an organic or aqueous solvent, to an already oriented polyester substrate, or more preferably before or during the stretching operation. Alternatively, the polyester ink-receptive layer may be formed by casting the ink-receptive polyester onto a preformed substrate layer. Conveniently, however, formation of a composite sheet (polyester substrate and polyester

ink-receptive layer) is effected by coextrusion, either by simultaneous coextrusion of the respective film-forming layers through independent orifices of a multi-orifice die, and thereafter uniting the still molten layers, or, preferably, by single-channel coextrusion in which molten streams of the respective polyesters are first united within  
5 a channel leading to a die manifold, and thereafter extruded together from the die orifice under conditions of streamline flow without intermixing thereby to produce a composite sheet.

A coextruded sheet is stretched to effect molecular orientation of the substrate, and preferably heat-set. Generally, the conditions applied for stretching the substrate  
10 layer will induce partial crystallisation of the ink-receptive polyester and it is therefore preferred to heat set under dimensional restraint at a temperature selected to develop the desired morphology of the ink-receptive layer. Thus, by effecting heat-setting at a temperature below the crystalline melting temperature of the ink-receptive polyester and permitting or causing the composite to cool, the ink-receptive polyester will remain  
15 essentially crystalline. However, by heat-setting at a temperature greater than the crystalline melting temperature of the ink-receptive polyester, the latter will be rendered essentially amorphous. Heat-setting of a composite sheet comprising a polyester substrate and a copolyester ink-receptive layer is conveniently effected at a temperature within a range of from 175 to 200°C to yield a substantially crystalline  
20 ink-receptive layer, or from 200 to 250°C to yield an essentially amorphous ink-receptive layer. An essentially amorphous ink-receptive layer is preferred.

In a preferred embodiment of the invention the polyester ink-receptive layer also exhibits heat-sealing properties, ie should be capable of forming a heat-seal bond to itself and/or to the polyester substrate and/or to the cover layer as described herein, by  
25 heating to soften the polyester material of the ink-receptive layer and applying pressure without softening or melting the polyester material of the substrate layer. The polyester ink-receptive layer preferably exhibits a heat-seal strength, measured by sealing the layer to itself, in the range from 300 to 3000, more preferably 1000 to 2500, and particularly 1800 to 2200 Nm<sup>-1</sup>.

30 The thickness of the polyester ink-receptive layer may vary over a wide range but generally will not exceed 50 µm, and is preferably within a range of from 0.5 to 25 µm, and more preferably from 3 to 15 µm.

In an alternative embodiment of the invention, the ink-receptive layer comprises an acrylic resin, by which is meant a resin which comprises at least one acrylic and/or  
35 methacrylic component.

The acrylic resin component of the ink-receptive layer is suitably thermoset and preferably comprises at least one monomer derived from an ester of acrylic acid and/or an ester of methacrylic acid, and/or derivatives thereof. In a preferred embodiment of the invention, the acrylic resin comprises greater than 50 mole %, preferably less than 5 98 mole %, more preferably in the range from 60 to 97 mole %, particularly 70 to 96 mole %, and especially 80 to 94 mole % of at least one monomer derived from an ester of acrylic acid and/or an ester of methacrylic acid, and/or derivatives thereof. A preferred acrylic resin comprises an alkyl ester of acrylic and/or methacrylic acid where the alkyl group contains up to ten carbon atoms such as methyl, ethyl, n-propyl, 10 isopropyl, n-butyl, isobutyl, terbutyl, hexyl, 2-ethylhexyl, heptyl, and n-octyl. Polymers derived from an alkyl acrylate, for example ethyl acrylate and butyl acrylate, together with an alkyl methacrylate are preferred. Polymers comprising ethyl acrylate and methyl methacrylate are particularly preferred. The acrylate monomer is preferably present in a proportion in the range from 30 to 65 mole %, and the methacrylate 15 monomer is preferably present in a proportion in the range from 20 to 60 mole %.

Other monomers which are suitable for use in the preparation of the acrylic resin of the ink-receptive layer, which may be preferably copolymerised as optional additional monomers together with esters of acrylic acid and/or methacrylic acid, and/or derivatives thereof, include acrylonitrile, methacrylonitrile, halo-substituted acrylonitrile, 20 halo-substituted methacrylonitrile, acrylamide, methacrylamide, N-methylol acrylamide, N-ethanol acrylamide, N-propanol acrylamide, N-methacrylamide, N-ethanol methacrylamide, N-methyl acrylamide, N-tertiary butyl acrylamide, hydroxyethyl methacrylate, glycidyl acrylate, glycidyl methacrylate, dimethylamino ethyl methacrylate, itaconic acid, itaconic anhydride and half esters of itaconic acid.

25 Other optional monomers of the acrylic ink-receptive layer polymer include vinyl esters such as vinyl acetate, vinyl chloroacetate and vinyl benzoate, vinyl pyridine, vinyl chloride, vinylidene chloride, maleic acid, maleic anhydride, styrene and derivatives of styrene such as chloro styrene, hydroxy styrene and alkylated styrenes, wherein the alkyl group contains from one to ten carbon atoms.

30 A preferred acrylic resin, derived from 3 monomers comprises 35 to 60 mole % of ethyl acrylate/30 to 55 mole % of methyl methacrylate/2 to 20 mole % of methacrylamide, and especially comprising approximate molar proportions 46/46/8% respectively of ethyl acrylate/methyl methacrylate/acrylamide or methacrylamide, the latter polymer being particularly effective when thermoset, for example in the presence 35 of about 25 weight % of a methylated melamine-formaldehyde resin.

A preferred acrylic resin, derived from 4 monomers comprises a copolymer comprising comonomers (a) 35 to 40 mole % alkyl acrylate, (b) 35 to 40 mole % alkyl methacrylate, (c) 10 to 15 mole % of a monomer containing a free carboxyl group, and (d) 15 to 20 mole % of a monomer containing a sulphonic acid group and/or a salt thereof. Ethyl acrylate is a particularly preferred monomer (a) and methyl methacrylate is a particularly preferred monomer (b). Monomer (c) containing a free carboxyl group, ie a carboxyl group other than those involved in the polymerisation reaction by which the copolymer is formed, suitably comprises a copolymerisable unsaturated carboxylic acid, and is preferably selected from acrylic acid, methacrylic acid, maleic acid, and/or itaconic acid; with acrylic acid and itaconic acid being particularly preferred. The sulphonic acid group monomer (d) may be present as the free acid and/or a salt thereof, for example as the ammonium, substituted ammonium, or an alkali metal, such as lithium, sodium or potassium, salt. The sulphonate group does not participate in the polymerisation reaction by which the adherent copolymer resin is formed. The sulphonic acid group monomer is preferably aromatic, and more preferably is p-styrene sulphonic acid and/or a salt thereof.

The weight average molecular weight of the acrylic resin can vary over a wide range but is preferably in the range from 10,000 to 10,000,000, and more preferably 50,000 to 200,000.

The acrylic resin component of the ink-receptive layer preferably comprises at least 30%, more preferably in the range from 40 to 99%, particularly 50 to 85%, and especially 70 to 80% by weight relative to the total weight of the ink-receptive layer. The acrylic resin is generally water-insoluble. The ink-receptive coating composition including the water-insoluble acrylic resin may nevertheless be applied to the polyester film substrate as an aqueous dispersion.

If desired, the acrylic ink-receptive layer coating composition may also contain a cross-linking agent which functions to cross-link the layer thereby improving adhesion to the polyester film substrate. Additionally, the cross-linking agent should preferably be capable of internal cross-linking in order to provide protection against solvent penetration. Suitable cross-linking agents may comprise epoxy resins, alkyd resins, amine derivatives such as hexamethoxymethyl melamine, and/or condensation products of an amine, eg melamine, diazine, urea, cyclic ethylene urea, cyclic propylene urea, thiourea, cyclic ethylene thiourea, alkyl melamines, aryl melamines, benzo guanamines, guanamines, alkyl guanamines and aryl guanamines, with an aldehyde, eg formaldehyde. A useful condensation product is that of melamine with formaldehyde. The condensation product may optionally be alkoxylated. The

cross-linking agent may suitably be used in amounts of up to 70%, preferably in the range from 1 to 60%, more preferably 15 to 50%, and especially 20 to 30% by weight relative to the total weight of the ink-receptive layer. A catalyst is also preferably employed to facilitate cross-linking action of the cross-linking agent. Preferred  
5 catalysts for cross-linking melamine formaldehyde include para toluene sulphonic acid, maleic acid stabilised by reaction with a base, morpholinium paratoluene sulphonate, and ammonium nitrate.

The acrylic ink-receptive layer coating composition may be applied before, during or after the stretching operation in the production of an oriented film. The  
10 coating composition is preferably applied to the film substrate between the two stages (longitudinal and transverse) of a thermoplastics polyester film biaxial stretching operation. Such a sequence of stretching and coating is suitable for the production of an ink-receptive layer coated linear polyester film, particularly polyethylene terephthalate film, substrate, which is preferably firstly stretched in the longitudinal  
15 direction over a series of rotating rollers, coated, and then stretched transversely in a stenter oven, preferably followed by heat setting.

An acrylic ink-receptive layer coated polyester, especially polyethylene terephthalate, substrate is suitably heated up to 240°C, preferably up to 220°C, in order to dry the aqueous medium, or the solvent in the case of solvent-applied compositions,  
20 and also to assist in coalescing and forming the coating into a continuous and uniform layer. The cross-linking of cross-linkable coating compositions is also achieved at such temperatures.

The acrylic ink-receptive layer coating composition is preferably applied to the polyester film substrate by any suitable conventional technique such as dip coating, bead coating, reverse roller coating or slot coating.  
25

The acrylic ink-receptive layer is preferably applied to the polyester film substrate at a dry coat weight in the range from 0.05 to 5 mgdm<sup>-2</sup>, especially 0.1 to 2.0 mgdm<sup>-2</sup>. The thickness of the dry acrylic ink-receptive layer is preferably less than 1.5 µm, more preferably in the range from 0.01 to 1.0 µm, and particularly 0.02 to 0.5 µm.

30 In a particularly preferred embodiment, the opaque polyester substrate has a polyester ink-receptive layer, as described herein, on a first surface thereof, and an acrylic ink-receptive layer, as described herein, on a second surface thereof.

The chemical composition of the cover layer component of a multilayer card, according to the present invention may vary over a wide range, and is suitably selected  
35 from materials which include polyester, such as polyethylene terephthalate and PETG, polycarbonate, polyolefin, polyvinyl chloride, ABS resin and/or paper. The cover layer

is preferably a self-supporting film. Indeed, the cover layer may even be the major contributor to the total thickness of the multilayer card. The function of the cover layer, in addition to the support it provides for the overall card, is to provide protection, including security, for example for the ink-receptive layer and the information contained thereon. The cover layer may have more than one layer, preferably is a multilayer

5 polymer film, and for example may be an opaque polyester substrate having an ink-receptive layer as described herein. A multilayer card may be formed by laminating together two or more opaque polyester films by means of heat-sealing their respective polyester ink-receptive layers. Alternatively, non-heat-sealing ink-receptive layers may

10 be laminated together by means of an additional adhesive layer. In a preferred embodiment of the invention the cover layer is transparent in order that the information contained on the ink-receptive layer can be visualised. A preferred card contains an opaque polyester substrate, an ink-receptive layer, and at least one transparent polyester cover layer having a heat-sealable or ink-receptive layer, whereby the card is

15 formed by heat-sealing together the respective ink-receptive layers. A particularly preferred card is an all polyester film structure, having the general structure as described in EP-A-0497483, the disclosure of which is incorporated herein by reference. The opaque polyester support film and dye receptive or printable receiver film of EP-A-0497483 are equivalent to the polyester substrate and ink-receptive layer

20 respectively of a multilayer card according to the present invention.

The multilayer card according to the present invention includes any of the multilayer structures disclosed in US-A-5407893, the disclosure of which is incorporated herein by reference. The biaxially oriented polyester film and image receiving layer (numbers 3 and 1 respectively in Figures 6 to 13) of US-A-5407893 are

25 equivalent to the polyester substrate and ink-receptive layer respectively of a multilayer card according to the present invention.

The multilayer card according to the present invention can be used to form any of the card structures known in the art, including identification cards, magnetic cards such as credit cards and pre-paid cards, smart cards which may have an electronic chip at

30 the surface or encapsulated, for example in epoxy material, inside the card (a so-called contactless smart card).

The multilayer card preferably has a thickness in the range from 150 to 1000  $\mu\text{m}$ , more preferably 200 to 900  $\mu\text{m}$ , particularly 250 to 850  $\mu\text{m}$ , and especially 650 to 840  $\mu\text{m}$ .

The multilayer card preferably has a length in the range from 70 to 100 mm, more preferably 80 to 90 mm, and particularly about 86 mm, and a width in the range from 40 to 70 mm, more preferably 50 to 60 mm, and particularly about 54.5 mm.

The multilayer card according to the present invention is preferably formed by a lamination process, by which is meant that two or more separate self-supporting film structures, which may themselves contain more than one layer, are brought together and joined by suitable means, including heat or adhesive, to form a card. An opaque polyester substrate having an ink-receptive layer on at least one surface thereof is a preferred first self-supporting film structure and a cover layer a preferred second self-supporting film structure.

For manufacturing purposes, it is generally desirable for a card comprising substrate, ink-receptive layer and cover layer to be coterminous along all edges. However, this is not always the case, and for example, the ink-receptive layer may cover only part of the substrate and the cover layer may be joined to the substrate in the regions where there is no ink-receptive layer, generally by means of an additional adhesive layer.

The layers of a multilayer card according to the present invention may, if desired, contain any of the additives conventionally employed in the manufacture of polymeric films. Thus, agents such as dyes, pigments, voiding agents, lubricants, anti-oxidants, anti-blocking agents, surface active agents, slip aids, gloss-improvers, prodegradants, ultra-violet light stabilisers, viscosity modifiers and dispersion stabilisers may be incorporated as appropriate.

The invention is illustrated by reference to the following drawings in which:

Figure 1 is a schematic sectional elevation, not to scale, of a multilayer card having an opaque polyester film substrate, ink-receptive layer and cover layer.

Figure 2 is a similar schematic elevation of a multilayer card shown in Figure 1, with an additional information carrying layer on the surface of the ink-receptive layer, underneath the cover layer.

Figure 3 is a similar schematic elevation of a multilayer card shown in Figure 2, with an additional ink-receptive layer and cover layer, on the second side of the substrate.

Referring to Figure 1 of the drawings, the multilayer card comprises an opaque polyester film substrate layer (1) having an ink-receptive layer (2) bonded to a first surface (3) of the substrate, and a transparent cover layer (4) bonded to the surface of the ink-receptive layer (5) remote from the substrate.



The film of Figure 2 additionally comprises an information carrying layer (6) on the surface (7) of the ink-receptive layer (2).

5 The film of Figure 3 additionally comprises a second ink-receptive layer (8) on the second surface (9) of the substrate layer (1), and a second cover layer (10) on the surface (11) of the second ink-receptive layer (8) remote from the substrate (1). The second cover layer (10) is a multilayer film comprising an opaque polyester substrate layer (12) having ink-receptive (or heat-sealable) layers (13 and 14) on both surfaces thereof.

10 In this specification the following test methods have been used to determine certain properties of the layers of the multilayer card and/or of the card itself:

(i) Transmission Optical Density (TOD)

TOD of the film was measured using a Macbeth Densitometer TD 902 (obtained from Dent and Woods Ltd, Basingstoke, UK) in transmission mode.

(ii) Whiteness Index and Yellowness Index

15 The whiteness index and yellowness index of the film was measured using a Colorgard System 2000, Model/45 (manufactured by Pacific Scientific) based on the principles described in ASTM D 313.

(iii) Heat-Seal Strength

20 A heat-seal was formed by positioning together and heating two ink-receptive layers present on opaque polyester substrate layers, at 140°C for ten seconds under a pressure of 275 kPa (40 psi). The sealed film was cooled to room temperature, and the heat-seal strength determined by measuring the force required under linear tension per unit width of seal to peel the layers of the film apart at a constant speed of 4.23 mm/second.

25 (iii) Delamination Susceptibility

Delamination susceptibility was measured using the following edge impact test. A multilayer card of dimensions 86 mm x 54.5 mm x 750 (or 640) µm was held upright in the hand and uniformly hit 10 times by means of one of the corner edges of the card on to a wooden table. The card was then examined for delamination and scored as  
30 excellent (no delamination), good (small signs of delamination), or poor (total delamination - the layers of the card clearly separated and could be easily peeled apart).

The invention is further illustrated by reference to the following examples.

Example 1

35 Separate streams of a substrate layer polymer of polyethylene terephthalate comprising 15% by weight, relative to the total weight of the substrate, of anatase

titanium dioxide having a volume distributed median particle diameter of 0.7  $\mu\text{m}$ , 8% by weight, relative to the total weight of the substrate, of Lomod ST4090A (copolyester ether, supplied by General Electric Corporation), and 460 ppm of optical brightener, and two outer ink-receptive layer polymers comprising a copolyester of 82 mole % ethylene terephthalate and 18 mole % ethylene isophthalate were supplied from separate extruders to a single channel coextrusion assembly. The polymer layers were extruded through a film-forming die onto a water cooled rotating, quenching drum to yield an amorphous cast composite extrudate. The cast extrudate was heated to a temperature of about 80°C and then stretched longitudinally at a forward draw ratio of 3.2:1. The composite sheet was passed into a stenter oven, where the sheet was dried and stretched in the sideways direction to approximately 3.4 times its original dimensions. The biaxially stretched composite sheet was heat set at a temperature of about 225°C. Final film thickness of the composite sheet was 150  $\mu\text{m}$ . The opaque substrate layer was 125  $\mu\text{m}$  thick, the two outer ink-receptive layers were both 12.5  $\mu\text{m}$  thick.

The composite sheet was subjected to the test procedures described herein and exhibited the following properties:

(i) Transmission Optical Density (TOD) = 1.2.

(ii) Whiteness Index = 98 units.

Yellowness Index = -0.9 units.

(iii) Heat-Seal Strength = 2000  $\text{Nm}^{-1}$ .

Items (i) and (ii) are essentially properties of the opaque substrate layer, as the ink-receptive layers make little or no contribution thereto. Item (iii) is a property of the ink-receptive layers.

Five of the composite sheets produced above were press laminated together at a temperature of 150°C for 90 seconds to form a laminated sheet of thickness 750  $\mu\text{m}$ . Multilayer cards of dimensions 86 mm x 54.5 mm were cut out from the laminated sheet, subjected to the edge impact test described herein and exhibited the following property:

(iv) Delamination Susceptibility = excellent (ie no delamination).

#### Example 2

This is a comparative example not according to the invention.

The procedure of Example 1 was repeated except that Lomod ST4090A was omitted from the substrate layer composition. The multilayer cards of dimensions 86 mm x 54.5 mm which were cut from the laminated sheet of thickness 750  $\mu\text{m}$  were subjected to the edge impact test described herein and exhibited the following property:

(iv) Delamination Susceptibility = poor (ie total delamination - the layers of the card clearly separated and could be easily peeled apart).

### Example 3

5 The procedure of Example 1 was repeated except that Lomod TE3040A (copolyesterether, supplied by General Electric Corporation) was used instead of Lomod ST4090A. The multilayer cards of dimensions 86 mm x 54.5 mm which were cut from the laminated sheet of thickness 750  $\mu\text{m}$  were subjected to the edge impact test described herein and exhibited the following property:

(iv) Delamination Susceptibility = good (small signs of delamination).

### 10 Example 4

The procedure of Example 1 was repeated except that the substrate contained a blue dye instead of optical brightener, had a single copolyester ink-receptive layer, and the surface of the monoaxially oriented polyethylene terephthalate substrate film was coated with an acrylic ink-receptive layer composition comprising the following ingredients:

Acrylic resin	163 ml
(46% w/w aqueous latex of methyl methacrylate/ethyl acrylate/methacrylamide : 46/46/8 mole %, with 25% by weight methoxylated melamine-formaldehyde)	
Ammonium nitrate	6 ml
(10% w/w aqueous solution)	
Demineralised water	to 2.5 litres

25 Final film thickness was 320  $\mu\text{m}$ . The opaque polyester substrate layer was 295  $\mu\text{m}$  thick, the copolyester ink-receptive layer was 25  $\mu\text{m}$  thick, and the dry coat weight of the acrylic ink-receptive layer was approximately 0.04  $\mu\text{m}$ .

The film exhibited the following properties:

(ii) Whiteness Index = 96 units.

Yellowness Index = -5.7 units.

30 Two of the composite sheets produced above were press laminated together at a temperature of 150°C for 90 seconds to form a laminated sheet of thickness 640  $\mu\text{m}$ .

The multilayer cards of dimensions 86 mm x 54.5 mm which were cut from the laminated sheet of thickness 640  $\mu\text{m}$  were subjected to the edge impact test described herein and exhibited the following property:

(iv) Delamination Susceptibility = excellent (ie no delamination).

Claims

1. A multilayer card comprising (i) an opaque polyester film substrate comprising in the range from 0.2 to 30% by weight, relative to the total weight of the substrate, of at least one copolyesterether, (ii) an ink-receptive layer on at least one surface of the substrate, and (iii) a cover layer on the surface of the ink-receptive layer and/or surface of the substrate.
2. A multilayer card according to claim 1 wherein the copolyesterether comprises at least one alkylene terephthalate.
3. A multilayer card according to either one of claims 1 and 2 wherein the copolyesterether comprises at least one poly(alkylene oxide) glycol.
4. A multilayer card according to any one of the preceding claims wherein the substrate comprises in the range from 5 to 25% by weight, relative to the total weight of the substrate, of an inorganic filler.
5. A multilayer card according to any one of the preceding claims wherein the ink-receptive layer comprises an acrylic resin.
6. A multilayer card according to any one of the preceding claims wherein the ink-receptive layer comprises a polyester resin.
7. A multilayer card according to any one of the preceding claims wherein the substrate has (i) an ink-receptive layer comprising an acrylic resin on a first surface thereof, and (ii) an ink-receptive layer comprising a polyester resin on a second surface thereof.
8. A method of producing a multilayer card which comprises forming an opaque substrate by extruding a layer of molten linear polyester comprising an opacifying agent and in the range from 0.2 to 30% by weight, relative to the total weight of the substrate, of at least one copolyesterether, quenching the extrudate, orienting the quenched extrudate in at least one direction, forming an ink receptive layer on at least one surface of the substrate, applying pictorial and/or written information on the surface of the ink-receptive layer, and forming a cover layer on the surface of the information carrying ink receptive layer and/or surface of the substrate.
9. A method according to claim 9 wherein the substrate and ink-receptive layer(s) are formed by coextrusion.
10. A method according to either one of claims 8 and 9 wherein the multilayer card is formed by laminating together two or more separate self-supporting film structures.

Fig.1.

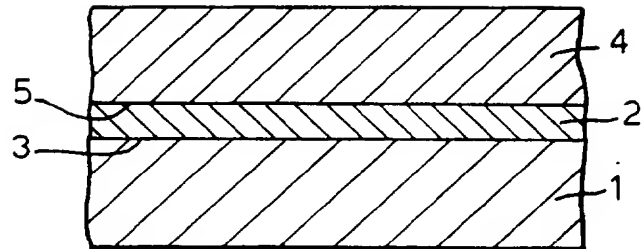


Fig.2.

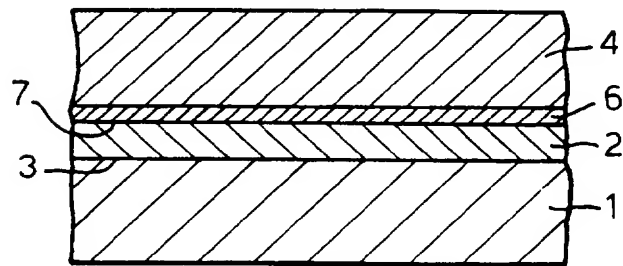
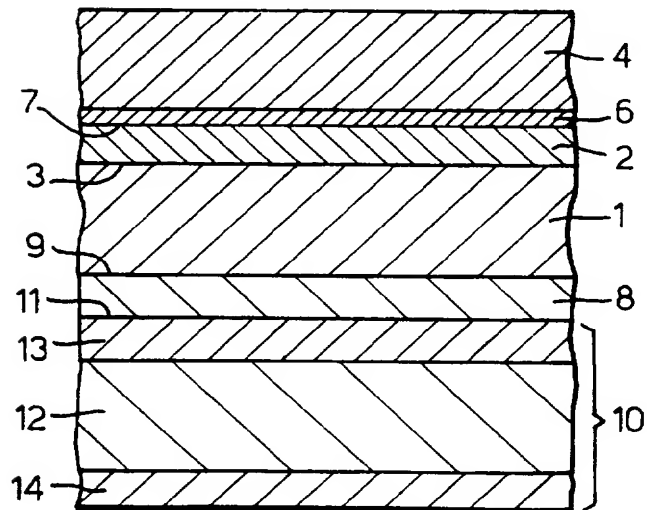


Fig.3.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/00708

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B32B27/36 B42D15/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B32B B42D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 497 483 A (ICI AMERICA INC) 5 August 1992 cited in the application see column 1, line 19 - column 2, line 1; claims	1-10
A	WO 95 10563 A (ICI PLC ;MILLS PAUL DAVID ALAN (GB); OLEK ANTON RICHARD (GB); RAKO) 20 April 1995 see page 1, line 1 - line 12; claims; figures	1-10
A	US 5 407 893 A (KOSHIZUKA KUNIHIRO ET AL) 18 April 1995 cited in the application see claims	1-10
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

16 July 1997

Date of mailing of the international search report

05. 08. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+ 31-70) 340-3016

Authorized officer

De Jonge, S

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/00708

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 437 942 A (ICI PLC) 24 July 1991  cited in the application  see claims  -----</p>	1



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/00708

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0497483 A	05-08-92	US 5171625 A AT 136255 T CA 2059982 A DE 69209544 D DE 69209544 T ES 2084928 T JP 4308749 A	15-12-92 15-04-96 01-08-92 09-05-96 12-09-96 16-05-96 30-10-92
WO 9510563 A	20-04-95	AU 7788994 A CA 2173614 A CN 1136322 A EP 0723565 A	04-05-95 20-04-95 20-11-96 31-07-96
US 5407893 A	18-04-95	NONE	
EP 0437942 A	24-07-91	AT 114326 T AU 629078 B AU 6812690 A CA 2032767 A CN 1054081 A DE 69014290 D DE 69014290 T JP 4211432 A	15-12-94 24-09-92 25-07-91 20-07-91 28-08-91 05-01-95 27-04-95 03-08-92